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Marine calcification as a source of carbon dioxide: Positive feedback of increasing atmospheric CO_2

Abstract—Calcification is a well-recognized source of CO_2 to the surrounding water and thus a potential source of atmospheric CO_2 due to chemical equilibria involving the CO_2 species. The *released CO_2: precipitated carbonate* ratio (Ψ) has recently been estimated to be 0.6 in seawater (taking into account the buffering capacity of the latter). We report an analytical expression enabling the computation of this ratio. Calculations show that the amount of CO_2 that must be released to equilibrate seawater increases with increasing partial pressure of CO_2 in seawater (pCO_2), which results from human impact on atmospheric CO_2. We show that at 15°C Ψ increased from 0.55 during the time of glaciation to 0.67 at present and would increase to 0.84 for a pCO_2 of 1,000 μatm. Doubling the preindustrial pCO_2 value results in a total CO_2 source of ~5 Gt C (taking into account the described buffering effect).

Understanding the global carbon cycle requires a better knowledge of C sinks and sources, but large uncertainties remain (Tans et al. 1990; Walsh 1991; Watson et al. 1991). One of these uncertainties concerns the effect of precipitation and dissolution of $CaCO_3$ on the cycling of marine carbon which causes difficulties in understanding the oceanic origins of the postglacial increase in CO_2 levels and in determining the global budget (Sundquist 1993). As a result of CO_2 chemical equilibria (e.g. Wollast et al. 1980), marine calcification is a sink for carbon which must take into account the fact that any carbonate—or bicarbonate—removal from seawater will induce an increase of the dissolved CO_2 level. Calcification therefore tends to drive CO_2 from the ocean to the atmosphere (Frankignoulle and

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Gattuso 1993; Gattuso et al. 1993). The *released CO_2 : precipitated carbonate* ratio (Ψ) was estimated to be 0.6 in seawater (using the present-day average CO_2 level of 350 μatm; Ware et al. 1992). This calculation was performed by simulating calcification in seawater in equilibrium with the atmosphere (open system) and looking at its effect on final CO_2 speciation. Ware et al. (1992) assumed that the rate of calcification equals half the decrease in total alkalinity and that air–sea CO_2 equilibrium occurs without alkalinity change.

A complete set of buffer factors for the seawater acid-base CO_2 system has recently been developed (Frankignoulle in press) which allows the calculation of changes in pCO_2 for any input-output of dissolved CO_2, carbonate, or bicarbonate ions. Calcification can proceed from carbonate ($Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3$) or bicarbonate ($Ca^{2+} + 2HCO_3^- + H_2O \rightleftharpoons CaCO_3 + CO_2 + H_2O$) ions, but the two equations have the same significance in terms of chemical dynamics. Both $\delta pCO_2/\delta(CO_2)$ and $\delta pCO_2/\delta(CO_3^{2-})$, where δ refers to infinitesimal variation and (CO_2) or (CO_3^{2-}) to the input-output of dissolved CO_2 or CO_3^{2-}, can then be computed under any physico-chemical condition. These buffer factors can be used to describe the dynamics of the seawater CO_2 system during calcification and to estimate the resulting release of CO_2.

Ψ can be analytically expressed by

$$\Psi = \frac{-(CO_2)}{(CO_3^{2-})} = -\left[\frac{\delta pCO_2}{\delta(CO_3^{2-})}\right]\left[\frac{\delta pCO_2}{\delta(CO_2)}\right]^{-1}$$

$$= -\frac{\{(R + 2QSa_H) \cdot [K_2A + PQ(a_H + K_2) + R(a_H/K_1)]\}}{RSQ^2}.$$

$$P = \frac{K_B TB}{(a_H + K_B)^2} + \frac{K_H}{a_H^2} + 1,$$

$$Q = a_H + 2K_2,$$

$$R = AQ + 2K_2A + PQa_H,$$

and

$$S = \frac{K_2A + PQ(a_H + K_2) + R\frac{a_H}{K_1}}{-Q\left(1 + \frac{2a_H}{K_1}\right)a_H}.$$

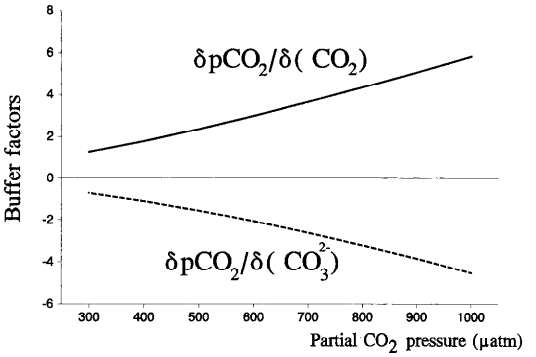

Fig. 1. Evolution of buffer factors describing the chemical dynamics of calcification vs. the partial CO_2 pressure in seawater. Buffer factors (in μatm kg mol^{-1}) give the change of pCO_2 resulting from the input and output of dissolved CO_2 or CO_3^{2-}. Calculations were carried out with the following values: total alkalinity = 2,400 μeq kg^{-1}, salinity = 35, temperature = 25°C, and chemical constants related to the NBS pH scale.

a_H is the proton H_3O^+ activity and A is the carbonate alkalinity, K_1 and K_2 are the CO_2 acidity constants, K_B is the borate acidity constant, K_H is the water acidity constant, and TB is the total boron concentration. Because the seawater pCO_2 is a function of both a_H and A values (Park 1969), a_H could be replaced in the above equations by $(K_1[HCO_3^-])/(pCO_2K_0)$, where K_0 is the CO_2 solubility coefficient and $[HCO_3^-]$ is the bicarbonate total concentration, thereby allowing calculations directly from pCO_2 data.

Ψ depends on the physicochemical properties of seawater and, as a result, on pCO_2, which has increased in surface seawater due to the burning of fossil C (Broecker and Peng 1982). The proposed equation for Ψ can be used to model the precipitation of carbonate from seawater. The effect of seawater pCO_2 on both buffer factors is shown in Fig. 1. The uptake of 1 mol of carbonate or of dissolved CO_2 at 25°C induces pCO_2 shifts of respectively +0.9 and −1.5 μatm when pCO_2 is 350 μatm. The shifts are +4.5 and −5.8 μatm when pCO_2 is 1,000 μatm. The associated Ψ is 0.6 when pCO_2 is 350 μatm, temperature is 25°C, and salinity is 35 (Fig. 2), which confirms the previous estimate obtained by numerical integration (Ware et al. 1992). Ψ rapidly increases when pCO_2 increases and reaches 0.78 for pCO_2 = 1,000 μatm. The amount of CO_2 released during calcification increases as a function of increasing

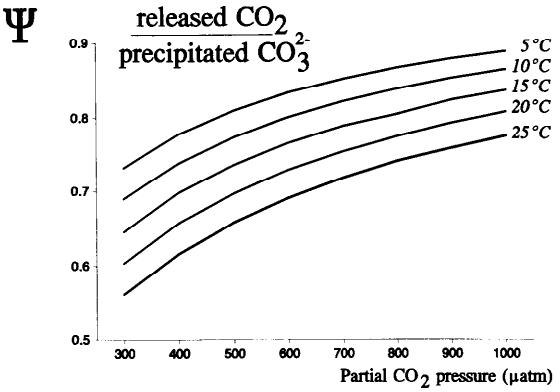

Fig. 2. Evolution of Ψ (in mol kg^{-1}) during the calcification process vs. the dissolved CO_2 level in seawater (salinity = 35 and total alkalinity = 2,400 μeq kg^{-1}, NBS pH scale).

seawater pCO_2 and the human-induced perturbation of the C cycle presents a positive feedback on the CO_2 release by marine calcification. The release of CO_2 induced by the calcification in shallow-water ecosystems (e.g. coral reefs) and by pelagic phytoplankton (coccolithophores) or zooplankton (pteropods, heteropods, and foraminifera) is clearly part of the current C cycle and natural greenhouse effect, but it is pointed out that, for pCO_2 higher than the preindustrial value, these organisms will increasingly participate in global change for purely thermodynamical reasons.

The preindustrial estimate of Ψ, calculated with a pCO_2 of 290 μatm, is 0.64 (t = 15°C, S = 35, total alkalinity = 2,400 μeq kg^{-1}); doubling the atmospheric pCO_2, as has been predicted to occur by about A.D. 2030–2050 (Perry 1982), will increase Ψ to 0.76. If we use the current estimate of annual carbonate production in open ocean and coastal zones (~1,000 Mt C yr^{-1}, Morse and Mackenzie 1990), doubling the pCO_2 in surface seawater would result in a net CO_2 source of ~130 Mt C yr^{-1} in 2030–2050. Calcification would, therefore, be an additional CO_2 source to the atmosphere representing ~2% of the present-day flux of fossil fuel. Integrating Ψ from 1880 to 2030–2050 (i.e. doubling of atmospheric pCO_2) shows that the total CO_2 released by the calcification in the ocean is of the order of 5 Gt C. Only ~20% of the precipitated carbonate will accumulate into the sediment (Morse and Mackenzie 1990), but the deep CO_2-consuming dissolution of this carbonate will occur under physicochemical conditions and Ψ values that should be fairly stable because of the short time scale relative to the response time of the deep ocean.

Figure 2 also shows that Ψ is highly negatively related to temperature (at pCO_2 = 350 μatm: $\Psi = 0.8\text{–}8.3 \times 10^{-3}\ t$, t in °C, $r^2 = 1$). As the greenhouse effect will cause warming of surface water, the increase of Ψ with pCO_2 would be smaller than at a constant temperature. So, doubling the preindustrial pCO_2 and warming the water by 3°C (Manabe and Wetherald 1980) will reduce Ψ to 0.74 rather than 0.76 as calculated above.

Ψ is also dependent on salinity and is ~1 in freshwater (Ware et al. 1992). Computation of Ψ as a function of salinity yields a linear relationship: $\Psi = 0.949\text{–}7.9 \times 10^{-3}\ S$ ($r^2 = 1$). This calculation has been carried out for salinities of 0–35 at a pCO_2 of 350 μatm, a temperature of 15°C, and total alkalinity varying linearly from 600 μeq kg^{-1} at S = 0 to 2,400 μeq kg^{-1} at S = 35.

The CO_2 released to seawater by calcification does not necessarily escape to the atmosphere. Air–sea CO_2 exchange has seldom been measured simultaneously with calcification, but some information is available for corals and coral reefs. Frankignoulle and Gattuso (1993) reported a ratio of CO_2 evasion to precipitated $CaCO_3$ of 0.1 by measuring the calcification rate in the laboratory of a zooxanthellate scleractinian coral and indirectly estimating the air–sea CO_2 fluxes. Direct measurements carried out at sea on a coral reef flat in Moorea (French Polynesia) showed that the ratio was 0.006 (Gattuso et al. 1993). The large difference between these ratios and Ψ (~0.6) can be attributed to several causes.

First, calcification occurs concomitantly with organic C metabolism. It is very difficult to separate the effects on the air–sea CO_2 fluxes of precipitation and dissolution of $CaCO_3$ from photosynthesis and respiration. For example, part of the CO_2 released by calcification can be taken up by photosynthetic processes before its evasion to the atmosphere, thereby decreasing the ratio of CO_2 evasion to precipitated $CaCO_3$. The very low measured ratios seem to agree with a tight coupling between organic

and inorganic C metabolism (Smith 1985, pers. comm.; Smith and Veeh 1989).

Second, the net effect of calcification on air–sea CO_2 exchange can be masked if the water entering a coral reef ecosystem is out of equilibrium with the atmosphere (*see* Gattuso et al. 1993); a high rate of calcification may not fully counterbalance a low oceanic pCO_2 and CO_2 invasion may still occur. Even when the ratio of CO_2 evasion to precipitated $CaCO_3$ is low due to the lock between calcification and photosynthesis and (or) to a pre-existing low pCO_2, a calcifying system remains a source of CO_2 to the atmosphere since it reduces the CO_2 invasion that would have occurred in a non-calcifying system.

Third, the estimation of the net effect of ecosystem metabolism on the CO_2 balance is not straightforward when the water residence time is brief (minutes to hours). Such conditions occur in reef flats because the gas exchange rate is low and equilibration processes continue after the reef crossing, and a full diel cycle is required to integrate the effect of all metabolic activities (i.e. photosynthetic CO_2 uptake and respiratory CO_2 release).

High $CaCO_3$ deposition in coral reefs (presently 111 Mt C yr^{-1}, Kinsey and Hopley 1991) is one of the mechanisms proposed to explain the increase of atmospheric CO_2 from 180 to 290 μatm during the last glacial-interglacial cycle. According to this "coral reef hypothesis," increased $CaCO_3$ deposition by coral reefs during sea-level rise released CO_2 to the upper ocean and the atmosphere (Berger 1982). It has been suggested (Opdyke and Walker 1992) that this hypothesis could account for first-order changes in atmospheric CO_2, although the ratio of released CO_2 to precipitated carbonate used in the model is not specified. Since Ψ increases by 15% (0.55–0.62) when pCO_2 increases from 180 to 290 μatm and temperature increases from 15 to 17°C (Broecker and Peng 1982), changes of Ψ as a function of pCO_2 should be taken into account in models predicting changes in atmospheric CO_2 content.

Michel Frankignoulle
Christine Canon

Université de Liège
Laboratoire d'Océanologie
Institut de chimie, Bât B6
B 4000 Sart Tilman, Belgium

Jean-Pierre Gattuso[1]

URA 1453 CNRS
Laboratoire EPHE/Biologie Marine
Université
F 66860 Perpignan Cedex, France

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[1] Present address: Observatoire Océanologique Européen, Centre Scientifique de Monaco, Ave. Saint-Martin, MC-98000 Monaco.

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Effects on the benthic diffusive boundary layer imposed by microelectrodes

Abstract—Oxygen microgradients and fluxes were studied in a 0.3–0.6-mm-thick diffusive boundary layer (DBL) of aquatic sediments by the use of O_2 microelectrodes with sensing tips of 5 μm. One microelectrode was introduced vertically from above while another was introduced along the same vertical axis from below, thus penetrating up through the sediment. Microelectrodes introduced from below did not alter the DBL, but those introduced from above reduced its thickness by 25–45%. The effect was detected even when the microsensor tip was situated >1 mm above the sediment surface. The reduction of the DBL resulted in steepening the O_2 gradient. In typical coastal sediments, the microelectrode thereby increased the diffusive O_2 flux by 8%; in a highly sulfidic sediment the increase was 59%.

The high spatial resolution of 2–10-μm-wide oxygen microelectrodes has enabled direct measurements of distribution and dynamics of O_2 in the diffusive boundary layer (DBL) (Jørgensen and Des Marais 1990). The DBL is a thin film of water that covers solid surfaces like sediments and through which the main transport of dissolved material is by diffusion. The change from a uniform distribution of solutes in the turbulent water phase to a linear diffusion gradient in the DBL is generally found 0.2–1.0 mm above the sediment surface (Santschi et al. 1983; Archer et al. 1989). Due to turbulence in the overlying water, the DBL is unstable and the O_2 concentration at any specific depth in the DBL therefore fluctuates (Gundersen and Jørgensen 1990). Despite the modest thickness of the DBL, it can play an important role in limiting fluxes of nutrients and gasses across the sediment–water interface (Boudreau and Guinasso 1982). Because particles at the sediment surface smaller than half the thickness of the DBL have no detectable effect on the surface topography of the DBL (Jørgensen and Revsbech 1985), it has been assumed that microelectrodes with tip diameter <10 μm do not affect the DBL structure.

We investigated this assumption by simultaneously introducing microelectrodes into the sediment–water interface from below and above.

We collected cores of fine-grained sediment (5.2–cm i.d.) at two stations in Aarhus Bight, Denmark (Rasmussen and Jørgensen 1992). Station A was characterized by a 2-cm-thick brown oxidized surface and station B was covered by mats of *Beggiatoa,* filamentous colorless sulfur bacteria that gain energy from the oxidation of H_2S with O_2 (Larkin and Strohl 1983).

To measure the effect on the DBL imposed by a microelectrode inserted from above, we made a transparent cylindrical Plexiglas chamber (Fig. 1). Microelectrodes could be introduced from below through 3-mm-wide holes in the bottom. The bottom and the holes were covered with a 10-mm layer of agar (1.5%) before adding a 15-mm slice of sediment 1 d

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